

Helsinki 14.5.2003

Rec PCT/PTO 20 SEP 2004 #2

PCT/FIO 3 / 0 0 2 0 8

ETUOIKEUSTODISTUS  
PRIORITY DOCUMENT

REC'D 10 JUN 2003

WIPO PCT



Hakija  
Applicant

Raisio Chemicals Oy  
Raisio

Patenttihakemus nro  
Patent application no

20020521

Tekemispäivä  
Filing date

19.03.2002

Kansainvälinen luokka  
International class

D21H

Keksinnön nimitys  
Title of invention

"Composition for surface treatment of paper and its use"  
(Paperin pintakäsittelykoostumus ja sen käyttö)

Täten todistetaan, että oheliset asiakirjat ovat tarkkoja jäljennöksiä Patentti- ja rekisterihallitukselle alkuaan annetuista selityksestä, patenttivaatimuksesta ja tiivistelmästä.

This is to certify that the annexed documents are true copies of the description, claims and abstract originally filed with the Finnish Patent Office.

*Marketta Tehikoski*

Marketta Tehikoski  
Apulaistarkastaja

**PRIORITY DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH  
RULE 17.1(a) OR (b)

Maksu 50 €  
Fee 50 EUR

Maksu perustuu kauppa- ja teollisuusministeriön antamaan asetukseen 1027/2001 Patentti- ja rekisterihallituksen maksullisista suoritteista muutoksineen.

The fee is based on the Decree with amendments of the Ministry of Trade and Industry No. 1027/2001 concerning the chargeable services of the National Board of Patents and Registration of Finland.

Osoite: Arkadiankatu 6 A  
P.O.Box 1160  
FIN-00101 Helsinki, FINLAND

Puhelin: 09 6939 500  
Telephone: + 358 9 6939 500

Telefax: 09 6939 5328  
Telefax: + 358 9 6939 5328

## COMPOSITION FOR SURFACE TREATMENT OF PAPER AND ITS USE

The present invention relates to a composition for surface treatment of paper, board or the like defined in the preambles of the independent claims presented hereafter, to a surface size composition, a method for surface treatment of paper, board or the like, use of surface treatment composition and to surface treated paper, board or the like.

During the last decennium the use of inkjet printing paper has been steadily increasing together with the increasing use of computers both at home and in the work. At the same time the need for reasonably priced quality inkjet printing paper has been growing. Computer users are interested in to print with normal office and home printers even more demanding documents, such as photos, where printing properties of the paper, like good resolution and minimal bleeding of ink, are of utmost importance. This, as well as the development of the printing technology, has put a strain on the printing properties of the inkjet printing paper.

Due to these market demands papermakers wish to improve the quality of their inkjet printing paper. Conventional ink jet printing papers can be roughly divided into two main groups, namely into surface sized printing paper and coated printing paper. The purpose of both surface sizing and coating is to affect the properties of the paper, such as its porosity, printability, smoothness and gloss.

Surface sized inkjet paper, such as normal office paper, is relatively cheap to produce, but its printing properties are poor as the ink easily penetrates into the paper, causing bleeding and loss of ink density and brightness. Surface sizing is usually carried out on-line in a sizing device fitted in the drying section of the paper machine, but it can also be carried out by means of a separate coating unit, e.g. when the paper machine does not have a surface sizing unit.

Surface size compositions are usually based on starch, carboxymethyl cellulose (CMC), polyvinyl alcohol, glucomannan, or water-soluble proteins. Mixtures of the above-mentioned substances can be also used. Starch can be native starch, degraded and/or chemically modified. Glucomannan can be in native form or chemically modified. Examples of protein that are used can be mentioned gelatin and casein, which can be in native form, or degraded and/or chemically modified.

Conventional coated inkjet printing paper has normally much better printing properties than the surface sized inkjet printing paper. Coating colour compositions comprise normally pigments, binders and additives. Coating is normally carried out by means of a separate coating unit, and the production costs are relatively high.

Nanoparticles, such as colloidal synthetic layered metal silica particles, has been used as pigment in coating colours for inkjet printing paper. Unfortunately nanoparticles are so small that they are easily carried into the base paper, where applied on the paper in conventional coating colours. When nanoparticles enter and accumulate the base paper they fail to function as intended, their effect on the surface properties of the paper being reduced. Also, when significant portion of applied nanoparticles is absorbed into the base paper, it is necessary to increase the amount of nanoparticles applied to achieve the desired surface properties. This results an unacceptable increase in coating costs. Accumulation of nanoparticles can also have a negative impact on paper properties, for example by increasing the penetration of liquid into the paper.

The object of the present invention is to provide an improved composition for surface treatment of paper, board or the like, by means of which the above-mentioned problems can be minimised or eliminated.

The object is thus to provide a surface treatment composition for paper, board or the like, by means of which the printing properties, especially ink jet printing properties, can be improved.

Another object of the present invention is to provide a surface size composition for  
5 paper, board or the like, by means of which especially the ink jet printing properties can be improved.

In order to achieve the above-mentioned objects the present invention is characterised in what is defined in the characterising parts of the independent claims presented hereafter.

10 A typical composition for surface treatment of paper, board or the like, according to the present invention comprises

- a nanoparticle fraction, and
- a carrier fraction comprising
  - plate-like pigment particles, and
  - 15 - at least one binder.

Typical composition for the surface sizing of paper, board or the like, according to the present invention comprises

- a surface size fraction comprising
  - a water-soluble main component, such as starch, polyvinyl alcohol, carboxy-  
20 methyl cellulose, glucomannan, protein, or a mixture thereof,
- and in addition
  - a nanoparticle fraction, and
  - a carrier fraction comprising
    - plate-like pigment particles, and
    - 25 - at least one binder.

Now it has been surprisingly found out that inkjet printing paper with good printing properties can be obtained when the paper is surface treated or surface sized with a composition comprising nanoparticles and a carrier fraction. Carrier fraction will help to detain the nanoparticles on the surface layer of the surface treated paper and inhibit the absorption and accumulation of the nanoparticles into the base paper. As the nanoparticles are captured in the surface layer formed during the surface treatment of the paper, they can give good surface properties for the paper, which is treated. This enables the production of inkjet printing paper, which has excellent printing properties, at reasonably low cost.

- 10 As the surface treatment according to the present invention can be carried out by means of conventional surface sizing unit, no expensive investments are needed for separate coating units. Paper mills, which today produce surface sized ink jet paper, can use their existing surface sizing equipment for surface treatment of paper according to the present invention. The present invention may therefore enable  
15 production of inkjet printing paper of high quality with low investment costs.

The present invention can be used for surface treatment or surface sizing of paper, board or other corresponding web-like materials produced from pulp. In the description the word "paper" has been used for reasons of legibility, but it should be understood to cover also board and/or other corresponding web-like materials  
20 produced from pulp.

The term "nanoparticle" when used in context of the present invention includes all kinds of pigment and/or mineral particles with size ranging from 5 to 500 nm. The nanoparticle size is preferably from 10 to 100 nm, more preferably from 15 to 50 nm. In some embodiments of the invention the nanoparticle size varies from 10  
25 to 200 nm, preferably from 15 to 75 nm. According to one preferred embodiment of the present invention the used nanoparticles are synthetic silica particles, such as

colloidal synthetic layered silicates, or precipitated calcium carbonate (PCC) nanoparticles or other corresponding nanoparticles.

The proportion of the nanoparticle fraction to the carrier fraction in the surface treatment composition according to present invention is typically 5/95 – 95/5, more typically 20/80 – 80/20, most typically 20/80 – 60/40, calculated as dry matter.

As the nanoparticles are small, a great number of them can exist in a thin layer. The present invention makes it possible to detain the nanoparticles in the surface layer of the surface treated paper. Therefore the number of nanoparticles in the surface layer can become high, even if the layer of the surface treatment composition itself on the paper surface is thin. This can enable sizing or coating of thinner surface layers, i.e. using smaller amount of surface treatment composition per square meter of paper. Good surface properties can still be obtained for surfaced treated paper due to the closely packed nanoparticles.

The plate-like or slate-like pigment particles in the carrier fraction of the present invention can be mineral particles, such as silicate particles, mica particles, kaolin particles, bentonite particles, alumina trihydrate particles, phyllosilicate particles, such as talc particles or organic pigment particles, such as plastic pigment particles. Preferably the plate-like pigment particles are kaolin particles or phyllosilicate particles, such as talc. The size of the pigment particles in the carrier fraction usually varies between 1 – 100  $\mu\text{m}$ , being typically under 50  $\mu\text{m}$ , being typically over 1  $\mu\text{m}$ . Frequently the size of the pigment particles in the carrier fraction varies between 1 – 10  $\mu\text{m}$ .

The plate-like pigment particles can detain the nanoparticles on the surface layer of the paper being surface treated, either by mechanical interactions or by physical interactions, or both. The size of the plate-like particles can be large enough to block the spaces between the fibres in the paper, i.e. they can reduce the paper

porosity, thus reducing absorption of nanoparticles in the base paper. The plate-like pigment particles can also detain nanoparticles by other interactions, such as physical and/or chemical interactions, for example by electrical forces.

- 5 As the plate-like pigment particles can capture the nanoparticles in the surface layer, the present invention can also reduce the total amount of nanoparticles, which are applied on the paper. With the present invention desired surface properties may be obtained by using smaller total amount of nanoparticles, as they will stay in the surface layer, and not be so highly absorbed in the base paper.

- 10 The proportion of the plate-like pigment particles in the carrier fraction of surface treatment composition is typically between 20 and 80 % of the solids content, more typically between 35 and 75 %, most typically between 40 and 70 %.

- 15 The carrier fraction comprises also at least one binder, such as polymer latex and/or other corresponding binder. Preferably the binder is polymer latex, such as styrene butadiene, acrylate, styrene acrylate or polyvinyl acetate latex or mixture thereof.
- 20 The binder can also be a water-soluble binder, either a derivative of natural polymers, such as starch, protein, carboxymethyl cellulose or other cellulose derivative, or a fully synthetic polymer, such as polyvinyl alcohol, or a mixture of different water-soluble binders. Proportion of the binder is preferably between 5 – 75 % of the solids content, more preferably between 15 – 45 %, most preferably between 20 – 40 %. The amount of binder is usually under 60 %.

According to another embodiment of the invention the surface treatment composition can also comprise a water-soluble component, such as starch, polyvinyl alcohol, carboxymethyl cellulose (CMC), glucomanan, protein, or their mixture.

According to another embodiment of the invention the composition for surface treatment of paper can comprise in addition to the nanoparticles and carrier fraction also one or more additional components, such as hydrophobic agents, antifoaming or defoaming agents and/or salts, surface tension agents, rheology modifiers, plasticising agents, lubricants, optical brightening agents, colouring agents and/or cross-linkers.

According to one preferred embodiment the nanoparticle fraction of the surface treatment composition comprises synthetic silica nanoparticles or precipitated calcium carbonate nanoparticles, and the carrier fraction comprises talc and/or kaolin as pigment particles and styrene-butadiene latex as a binder.

Surface size composition according to one embodiment of the present invention comprises a surface size fraction, known *per se*, and a nanoparticle fraction and a carrier fraction for detaining the nanoparticles in the surface layer. The carrier fraction comprises plate-like or platy pigment particles and a binder. In the surface size composition the proportion of the surface size fraction to the sum of the nanoparticle and carrier fractions, calculated as dry matter, is typically 20/80 – 80/20, more typically 20/80 – 50/50.

Surface size composition according to one embodiment of the present invention can be prepared simply by mixing together the nanoparticle and carrier fractions so that they form a relatively homogenous mixture. This mixture is then added to a surface size fraction, known *per se*.

According to another embodiment of the invention the nanoparticle and carrier fractions can be mixed independently with the surface size fraction. In that case it is not necessary to mix first the nanoparticle fraction with the carrier fraction before addition to the surface size fraction. The carrier fraction comprising platy pigment particles can be mixed first to the surface size and then the nanoparticle fraction can



be added to this mixture containing surface size and carrier particles. Carrier and nanoparticle fractions can also be added to the surface size fraction alternately, or separately and independently at the same time.

According to the present invention in a typical surface treatment method of paper, board or the like, the paper is treated by applying to the paper surface a composition comprising a nanoparticle fraction, and a carrier fraction, which comprises a plate-like pigment particles and at least one binder. The carrier fraction will help to detain the nanoparticles in the surface layer of the surface treated paper.

Surface treatment of paper according to the present invention is preferably carried out by means of conventional surface treatment unit, such as size press, film press or the like. If coating units are available, surface treatment can be carried out in them. Coating units can be either separate or integrated to the paper machine, i.e. on-line coating units.

According to one preferred embodiment of the present invention the surface treatment composition is applied on the paper web when the dry matter of the web is  $\geq 75\%$ , preferably  $\geq 85\%$ , most preferably  $\geq 90\%$ .

Surface treatment of paper according to the present invention encompasses surface sizing, pigmentising, coating and other similar surface treatments of paper. According to one preferred embodiment of the present invention the surface treatment composition is used for surface sizing of paper. The compositions according the present invention can also be used for other surface treatment, for example for coating of paper.

Preferably the composition for surface treatment of paper according to present invention can be applied by means of already existing machines for surface treatment of paper. The amount applied is typically  $1.5 - 10 \text{ g/m}^2$ , more typically 3

- 6 g/m<sup>2</sup> of surface treatment composition, calculated as dry, per side. Also larger or smaller amounts can be applied if necessary.

According to one embodiment of the present invention the printing properties of the paper that has been surface treated or surface sized will closely match the printing  
5 properties of matte coated inkjet printing paper. Use of a composition according the present invention in paper coating can also enhance the properties of coated paper when compared to papers coated with conventional coating colours.

According to one preferred embodiment of the present invention the surface treatment composition is applied on the surface of inkjet printing paper or release  
10 paper. The present invention enables the production of smooth paper surface and enhances the printing properties of office paper. In release paper the smooth surface and low porosity can help to minimise the amount of silicone used in siliconising.

The surface treatment composition according to present invention can be also used for surface treatment of other ink jet recording material, such as plastic films. It can  
15 be also used for surface treatment of other paper-like materials or board.

The present invention is further illustrated by the following non-limiting examples. The materials are given as amounts of solids content, if not otherwise stated.

#### Example 1

A carrier fraction was prepared by mixing 64.4 % talc granulates, 34.8 % styrene-butadiene latex, 0.5 % antifoaming agent and 0.3 % dispersing agent and water in a  
20 mixer. After the mixing the solid content of the carrier fraction was adjusted to 45 % with water.

10.

The carrier fraction was then further mixed in a mixer with a nanoparticle fraction (in slurry form) in proportion 50/50 in order to obtain a composition for surface treatment of paper. As nanoparticles synthetic silicate particles having a mean particle size around 25 nm were used. The solid content was adjusted to 20 % with water.

The obtained surface treatment composition was then added to a starch solution (solids content 15 %). The proportion of the starch solution to the surface treatment composition was 50/50. This mixture was then applied on a paper surface in amount 5 g/m<sup>2</sup> in a film transfer unit.

## 10 Example 2

A carrier fraction was prepared by mixing 67.5 % talc slurry (solids content 60 %), 30 % styrene-acrylate latex, 2 % plasticising agent, 0.4 % antifoaming agent and 0.1 dispersing agent in a mixer. After the mixing the dry solids content of the carrier fraction was adjusted to 55 %.

15 The carrier fraction was then further mixed in a mixer with a nanoparticle fraction (in slurry form) in proportion 70/30 to obtain a composition for surface treatment of paper. As nanoparticles synthetic silicate particles having a mean particle size around 25 nm were used. The solid content was adjusted to 20 % with water.

20 The obtained surface treatment composition was then added to polyvinyl alcohol (PVA) solution (solids content 20 %). The proportion of the PVA solution to the surface treatment composition was 80/20. This mixture was then applied on a paper surface in amount 4.5 g/m<sup>2</sup> by using rod coater unit.

## Example 3

A carrier fraction was prepared by mixing 65 % polyvinyl alcohol, 20 % kaolin, 10 % CMC and 5 % hardening agent in a mixer. After mixing the solids content of the carrier fraction was adjusted to 15 %.

The carrier fraction was then further mixed in a mixer with a nanoparticle fraction (in slurry form) in proportion 93/7 to obtain a composition for surface treatment of paper. As nanoparticles synthetic silicate particles having a mean particle size around 25 nm were used. The solid content was adjusted to 15 % with water.

The obtained surface treatment composition was then applied directly on a paper surface in amount 2 g/m<sup>2</sup> in a size press unit.

10 Papers, which were surface treated according to examples 1 – 3, were evaluated both by visual evaluation and by using time-of-flight secondary-ion mass spectrometry (TOF-SIMS).

In visual evaluation it was discovered that the ink jet printing properties of the papers surface treated with surface treatment compositions according to examples 1 – 3 was much better than printing properties of conventional office ink jet papers. The printing quality was much even and the colours were brighter.

By using TOF-SIMS a certain chemical elements that originate from nanoparticles were detected on the paper surface. It was discovered that papers surface treated according to examples 1 – 3 the amount of these elements was significantly higher than in papers coated with nanoparticles without carrier fraction. This indicates that the carrier fraction in the surface composition according to present invention effectively detains the nanoparticles in the surface layer of the paper.

The compositions for surface treatment and for surface sizing of paper according present invention enable therefore production of inkjet printing paper with excellent

ink jet printing properties. These superior printing properties can be obtained at relatively low cost, when the surface treatment composition can be applied at conventional surface sizing units.

5 When using the present invention for coating of paper the amount of coating colour needed per square unit of paper is reduced, as the nanoparticles are detained in the surface layer and not absorbed by the base paper. This will help to reduce the coating costs, because a smaller amount of the coating colour is needed in order to still obtain good surface properties.

10 It will be appreciated that the essence of the present invention can be incorporated in the form of a variety of embodiments, only a few of which are disclosed herein. It will be apparent for the specialist in the field that other embodiments exist and do not depart from the spirit of the invention. Thus, the described embodiments are illustrative and should not be construed as restrictive.

L 2

13

**Claims**

1. Composition for surface treatment of paper, board or the like, characterised in that the composition comprises

- a nanoparticle fraction, and
- 5 - a carrier fraction comprising
  - plate-like pigment particles, and
  - at least one binder.

2. Composition for the surface sizing of paper, board or the like comprising a surface size fraction comprising

- 10 - a water-soluble main component, such as starch, polyvinyl alcohol, carboxymethyl cellulose, glucomannan, protein, or a mixture thereof,

characterised in that

composition for surface sizing comprises in addition to the surface size fraction

- a nanoparticle fraction, and
- 15 - a carrier fraction comprising
  - plate-like pigment particles, and
  - at least one binder.

3. Composition according to claim 1 or 2, characterised in that the pigment particles in the carrier fraction comprise mineral particles, such as silicate particles, mica particles, kaolin particles, bentonite particles, alumina trihydrate particles, phyllosilicate particles, such as talc particles, or organic pigment particles, such as plastic pigment particles.

4. Composition according to claim 3, characterised in that the pigment particles in the carrier fraction are kaolin particles or phyllosilicate particles, such as talc.

5. Composition according to claim 1 or 2, characterised in that the binder in the carrier fraction is a polymer latex and/or other corresponding binder.

6. Composition according to claim 5, characterised in that the binder in the carrier fraction is styrene butadiene, acrylate, styrene acrylate or polyvinyl acetate latex or  
5 mixture thereof.

7. Composition according to claim 1 or 2, characterised in that the nanoparticles comprise synthetic silica particles, precipitated calcium carbonate particles, or other corresponding nanoparticles.

8. Composition according to claim 1 or 2, characterised in that the nanoparticle  
10 size is 5 – 500 nm, preferably 10 – 100 nm, more preferably 15 – 50 nm.

9. Composition according to claim 1 or 2, characterised in that proportion of the nanoparticle fraction to the carrier fraction is typically 5/95 – 95/5, more typically 20/80 – 80/20, most typically 20/80 – 60/40, calculated as dry matter.

10. Composition according to claim 1 or 2, characterised in that the proportion of  
15 the plate-like pigment particles in the carrier fraction is typically between 20 and 80 % of the solids content, more typically between 35 and 75 %, most typically between 40 and 70 %.

11. Composition according to claim 1 or 2, characterised in that the proportion of  
20 the binder in the carrier fraction is typically 5 – 75 %, more typically 15 – 45 %, most typically between 20 – 40 % of the solids content.

12. Composition according to claim 1 or 2, characterised in that the composition comprises in addition one or more additional components, such as hydrophobic agents, antifoaming or defoaming agents and/or salts, surface tension agents,

rheology modifiers, plasticising agents, lubricants, optical brightening agents, colouring agents and/or cross-linkers.

13. Composition according to claim 1, characterised in that the composition also comprises a water-soluble component, such as starch, polyvinyl alcohol, carboxy-methyl cellulose, glucomannan, protein, or a mixture thereof.

14. Composition according to claim 1, characterised in that

- the nanoparticle fraction comprises synthetic silica particles or precipitated calcium carbonate particles,
- the carrier fraction comprises
  - talc and/or kaolin particles,
  - and styrene-butadiene latex.

15. Composition according to claim 2, characterised in that the nanoparticle fraction and the carrier fraction are mixed together before addition to the surface size fraction.

16. Composition according to claim 2, characterised in that the nanoparticle fraction and the carrier fraction are mixed independently with the surface size fraction.

17. Composition according to claim 2, characterised in that the proportion of the surface size fraction to the sum of the nanoparticle and carrier fractions, calculated as dry matter, is typically 20/80 – 80/20, more typically 20/80 – 50/50.

18. Method for surface treatment of paper characterised in that the paper, board or the like, is treated by applying to the paper surface a composition comprising

- a nanoparticle fraction, and
- a carrier fraction comprising



16

- a plate-like pigment particles, and
- at least one binder.

19. Method according to claim 18, characterised in that the composition is applied by means of a surface treatment unit, such as size press, film press or a coating unit.

5 20. Method according to claim 18, characterised in that the composition is applied on the web of paper, board or the like, when the dry matter of the web is  $\geq 75\%$ , preferably  $\geq 85\%$ , most preferably  $\geq 90\%$ .

21. Method according to claim 18, characterised in that the amount applied is preferably  $1.5 - 10 \text{ g/m}^2$ , more preferably  $3 - 6 \text{ g/m}^2$  of surface treatment  
10 composition, calculated as dry matter, per side.

22. Use of composition for surface treatment or for surface sizing according to any of the claims 1 - 17 for surface treatment of paper, board or the like.

23. Surface treated paper, board or the like characterised in that in the surface treatment is used composition for surface treatment or composition for surface  
15 sizing according to any of the claims 1 - 17.

L 3

**(57) Abstract**

Invention relates to a composition for surface treatment of paper. The composition for surface treatment of paper comprises a nanoparticle fraction, and a carrier fraction for  
5 detaining the nanoparticles in the surface layer. The carrier fraction comprises plate-like pigment particles, and at least one binder. The invention relates also to use of surface treatment composition.